ON THE THERMOELECTRIC EFFECT OF INTERFACE IMPERFECTIONS

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INTRODUCTION

Ordinary thermocouples use the well-known Seebeck effect to measure the temperature at the junction of two different conductors. The electromotive force generated by the heat depends on the difference between the respective thermoelectric powers of the contacting metals and the junction temperature. Figure 1 shows the schematic diagram of the thermoelectric measurement as most often used in nondestructive materials characterization. One of the reference electrodes is heated by electrical means to a preset temperature of 100 – 300 ^{o}C, pretty much like the tip of a temperature-stabilized soldering iron, and connected to the inverting (-) input of the differential amplifier driving the indicator. The other electrode is left cold at essentially room temperature and connected to the non-inverting (+) input. The measurement is done quickly in a few seconds to assure (i) that the hot reference electrode is not cooled down perceivably by the specimen and (ii) that the rest of the specimen beyond the close vicinity of the contact point is not warmed up perceivably. Ideally, regardless of the temperature difference between the junctions, only thermocouples made of different materials, i.e., materials of different thermoelectric power, will generate thermoelectric signal. This unique feature makes the simple thermoelectric tester one of the most sensitive material discriminators used in nondestructive inspection.

The thermoelectric power of metals is sensitive to a variety of material properties that can affect the measurement. Clearly, chemical composition exerts the strongest effect on the thermoelectric properties and accordingly the basic application of thermoelectric materials characterization is metal sorting [1]. However, it is known that under special conditions materials of identical chemical composition can also produce an efficient thermocouple as a result of different heat treatments, hardening, texture, fatigue, etc., which can be further exploited for nondestructive testing of materials [2-7]. A circuit composed of a single homogeneous conductor cannot produce a thermoelectric voltage. It is important to emphasize that, in this context, homogeneous means perfectly uniform throughout. Even a chemically perfectly homogeneous sample made of an isotropic material can be inhomogeneous because of strain. For example, annealed and cold-worked

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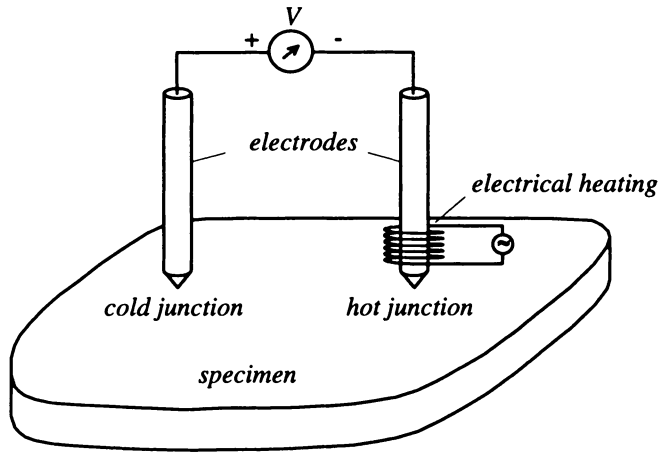

Figure 1. Schematic diagram of the thermoelectric measurement as most often used in nondestructive materials characterization.

copper was shown to form a rather sensitive thermocouple [8]. An additional effect can occur in a noncubic material like titanium, where individual grains exhibit anisotropic thermoelectric properties. As a result, coarse grain structure translates into apparent inhomogeneity and preferred orientation called texture can cause apparent macroscopic anisotropy [9].

EXPERIMENTAL TECHNIQUE

Let us consider the conventional thermoelectric technique previously shown in Figure 1. Because of inevitable uncertainties in the junction temperature on the order of approximately $\pm 5\%$, the thermoelectric voltage V_{SR}, and consequently the experimentally determined relative thermoelectric power S_{SR} are also uncertain within the same relative limits. The fundamental assumption in nondestructive thermoelectric testing is that, although the measured voltage is somewhat uncertain because of inevitable variations in the contact temperature, identical materials do not produce any thermoelectric voltage. Consequently, small differences in the thermoelectric power can be unequivocally detected only by using a reference electrode very similar to the material to be tested. Ideally, the thermoelectric power of the reference electrode should be somewhere halfway between those of the extreme materials to be distinguished so that they produce thermoelectric signals of opposite signs. In an effort to apply this simple strategy to optimize a commercially available thermoelectric tester for texture and fatigue damage detection in titanium alloys, we recognized that a considerable thermoelectric voltage could be measured even when the reference electrodes were made from the very same material as the specimen to be tested [10]. In the following we first present a few examples showing different degrees of thermoelectric offset and then investigate the physical reasons for this unexpected and previously unreported artifact which seriously limits the sensitivity of the thermoelectric technique to small variations in material properties.

Figure 2 shows examples of the thermoelectric signals measured at $T_i \approx 300\ ^{\circ}C$ between identical "specimen" and "reference" electrodes cut from the same thin wires of 1-1.5 mm in diameter for seven different materials. The schematic diagram of the experimental arrangement (with the reference electrode heated) is shown in Figure 3. Both electrodes were of sufficient length to assure that the far ends that were connected to a

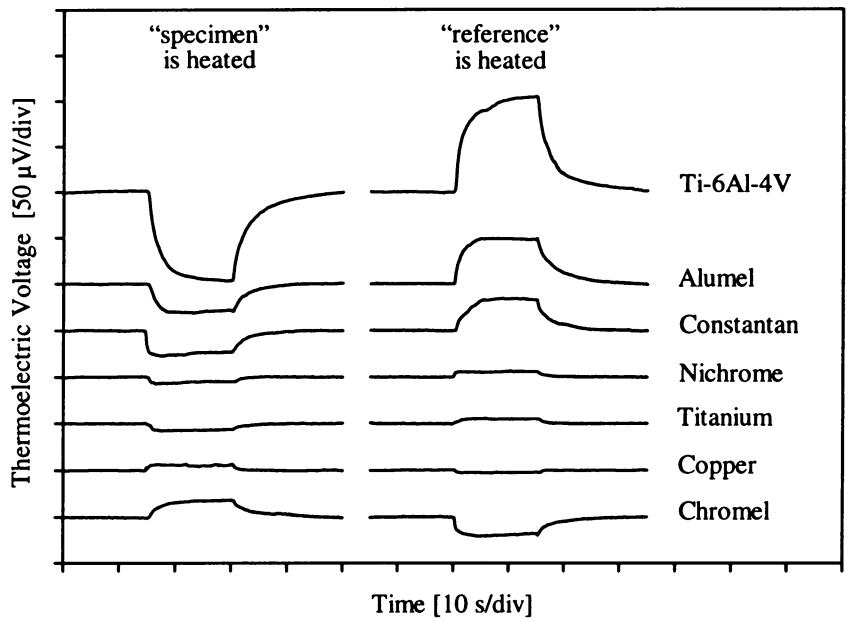

Figure 2. Examples of thermoelectric signals from seven thermocouples formed by two identical metals compressed together ($T_i \approx 300\ ^{o}C$).

differential amplifier were cold, i.e., remained at room temperature. By definition, the wire connected to the non-inverting input of the amplifier was considered to be the "specimen" and the one connected to the inverting input was the "reference" electrode. In spite of using identical materials for both electrodes, a significant thermoelectric signal was detectable in most cases. The measured thermoelectric signal was of basically the same amplitude but opposite sign for heating at the opposite sides of the junction. In comparison, when the junction was directly cooled by a FreezIt® spray so that neither positive nor negative temperature gradient could occur through the interface, no thermoelectric signal appeared

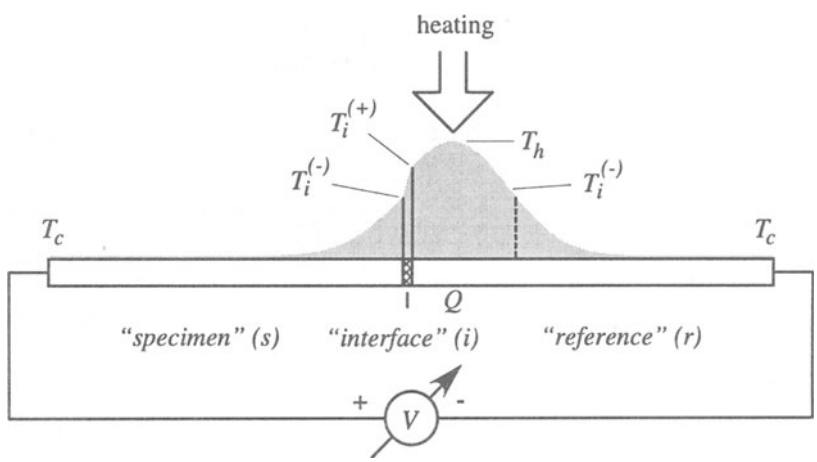

Figure 3. The model used in analyzing the thermoelectric offset produced by an imperfect interface between the heated reference electrode and the specimen to be tested.

between two identical wires. It should be mentioned that, like in essentially all thermoelectric nondestructive testing applications, the junction was formed by simply compressing rather than metallurgically bonding the electrodes. It was also noticed that the thermoelectric signal could be somewhat reduced but never completely eliminated by increasing the compressive pressure between the electrodes. Of course when the specimen and the reference electrode were parts of the same uncut wire, no thermoelectric signal was observed.

In order to understand the experimentally observed thermoelectric offset we must consider how the measured thermoelectric signal is produced as a result of the intrinsically coupled transport of electricity and heat via electron diffusion and phonon drag. Let us consider the simple thermoelectric circuit previously shown in Figure 3. The electrical potential difference V_{SR} between points S and R of constant ambient temperature $T_S = T_R = T_c$ is

$$V_{SR} = \int_{T_c}^{T_i^{(-)}} S_S(T)\,dT + \int_{T_i^{(-)}}^{T_i^{(+)}} S_i(T)\,dT + \int_{T_i^{(+)}}^{T_i^{(-)}} S_R(T)\,dT + \int_{T_i^{(-)}}^{T_c} S_R(T)\,dT, \qquad (1)$$

where S_S and S_R are the thermopowers of the specimen and the reference electrode, respectively, $T_i^{(-)}$ and $T_i^{(+)}$ denote the temperature on the colder and warmer sides of the interface, respectively, and S_i is the unknown effective thermoelectric power of the imperfect interface. The third and fourth terms on the right side of Eq. (1) were separated this way to conveniently approximate the thermoelectric voltage as follows

$$V_{SR} \approx \int_{T_c}^{T_i} [S_S(T) - S_R(T)]\,dT + [S_i(T_i) - S_R(T_i)]\,\Delta T_i, \qquad (2)$$

where $\Delta T_i = T_i^{(+)} - T_i^{(-)}$ denotes the temperature drop at the imperfect interface. Beside the well-known first term, Eq. (2) also contains a correction term related to the temperature gradient at the interface. Without this correction term, the thermoelectric voltage V_{SR} is zero regardless of the shape and size of the specimen as long as it is homogeneous and isotropic, i.e., $S_S(T) = S_R(T)$. Let us assume that the "reference" electrode is heated by a short thermal pulse at a point Q close to the interface as shown in Figure 3 so that $T_Q > T_S, T_R$ and consider the instantaneous thermoelectric voltage only so that neither T_S nor T_R has changed yet from their identical initial value of T_c. Clearly, $V_{SR} = V_{SQ} - V_{RQ} = 0$ because V_{SQ} is identical to V_{RQ}. In reality, the thermoelectric voltage will not completely vanish because of the presence of the imperfect interface between the "reference" and "specimen" electrodes.

An imperfect interface between contacting but metallurgically not bonded surfaces usually causes both reduced electrical and thermal conductivities, although the relative drop in the electrical conductivity tends to be larger than the corresponding drop in the thermal conductivity. Based on this general rule, the simplest physical approximation would be that $S_i << S_R$, and consequently the thermoelectric offset caused by the imperfect interface should be of opposite sign to the thermoelectric power of the reference material, $V_{SR} \approx -S_R(T_i)\,\Delta T_i$. At room temperature, S_R is negative for Ti-6Al-4V,

Alumel, and Constantan but positive for Chromel, Nichrome, Titanium, and Copper. A comparison with Figure 2 reveals that the measured thermoelectric offset was indeed of opposite sign to the thermoelectric power of the reference material in all the strongest cases. However, in the complex world of thermoelectricity simple models and approximations often fail to properly predict even the sign let alone the magnitude of the measured thermoelectric voltage. In the cases of Nichrome and pure Titanium, the much smaller but still measurable offsets were of the same sign as the thermoelectric power of the reference material. By far the strongest thermoelectric offset was exhibited by Ti-6Al-4V, the most popular titanium alloy used in the aerospace industry, that led us to our observation in the first place. The measured $\pm 100\mu V$ offset represents more than $\pm 0.3\mu V/^{o}C$ error in the thermoelectric power of Ti-6Al-4V, which is approximately $-4.9\mu V/^{o}C$ at room temperature [11]. Unless special measures are taken to eliminate this offset, conventional nondestructive thermoelectric techniques will not be able to detect the substantially weaker effects of fatigue, residual stress, texture, etc., in Ti-6Al-4V alloys.

EXPERIMENTAL RESULTS

In the following we demonstrate that the above described thermoelectric voltage of the imperfect interface between the specimen and the reference electrode can render conventional thermoelectric material testers insensitive to small material variations. In contrast, symmetric heating or cooling, that does not produce a significant thermal gradient through the interface, completely eliminates the problem. Figure 4 shows the results of a series of experiments on thermoelectric assessment of texture in Ti-6Al-4V alloy. This forged specimen exhibited a very strong anisotropic texture caused by the existence of a preferred crystallographic orientation in the polycrystalline structure that resulted in as much as 6% relative shear wave birefringence. In addition to this mechanical anisotropy, due to the dominantly hexagonal grain structure, the specimen also exhibited perceivable electrical conductivity anisotropy and was expected to show substantial thermoelectric anisotropy as well [12]. First, a commercial TE-3000 Koslow alloy sorter was used, which has a copper alloy reference electrode ($\approx +1.5\mu V/^{o}C$) heated to approximately 90° C (Figure 4a). Since the reference electrode was very different from the titanium specimen to be tested, all sides registered at around $-500\ \mu V$ and sides 1&3 could not be distinguished from 2&4. The observed large ($\approx \pm 10\%$) scatter in the data is primarily due to the uncertainty of the actual interface temperature between the titanium specimen and the copper reference electrode. Better separation was expected by using a reference electrode of similar thermoelectric coefficient to those of the specimens to be distinguished and increasing the temperature to assure sufficient sensitivity. Figure 4b shows the results obtained with a Ti-6Al-4V wire reference electrode heated to $\approx 300\ ^{o}C$. This method slightly improved the separation between sides 1&3 and 2&4 with respect to the measurements using the copper reference, but far less than one would have expect based on the choice of the reference electrode. The main reason for the experimental uncertainty is the approximately $+ 100\mu V \pm 10\%$ offset caused by the imperfect interface, which was previously shown to exist between even two identical Ti-6Al-4V wires (see Figure 2).

As we have mentioned above, the interface effect can be eliminated if the junction between the specimen and the reference electrode is heated or cooled at the same time on both sides, which assures that there is no temperature gradient through the interface. Instead of heating, we used a commercial FreezIt® 2000 cooling spray to cool the interface region to approximately $-70\ ^{o}C$. First, a Ti-6Al-4V wire was randomly chosen as a reference electrode (see Figure 4c). As expected, the large interface offset disappeared and

we could separate sides 1&3 and 2&4. However, both sides gave positive readings, which means that the thermoelectric coefficient of the randomly chosen Ti-6Al-4V wire was beyond those of the two textured sides. Since the interface temperature produced by cooling is highly variable, it would be much better if the reference electrode were between the two sides to be distinguished so that it would produce thermoelectric signals of

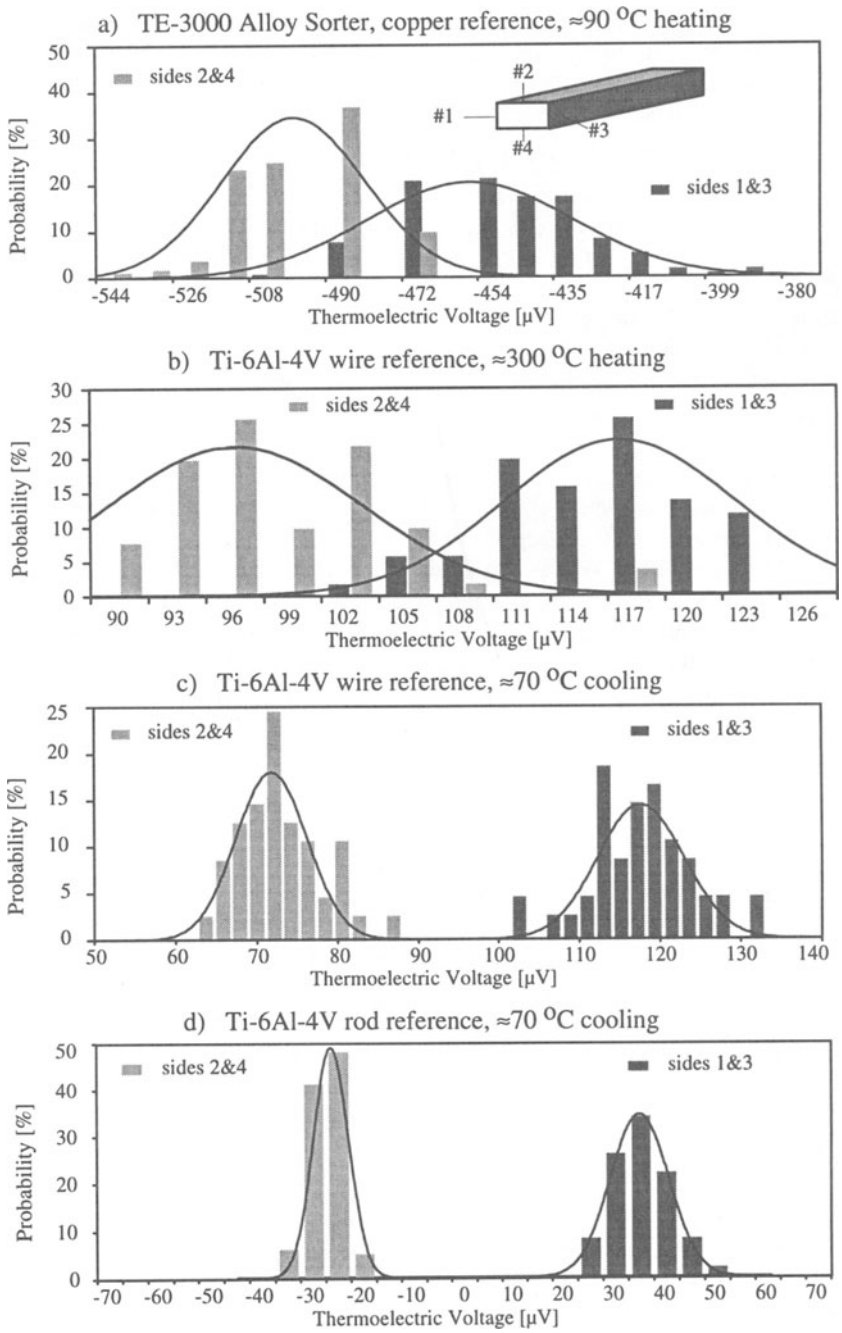

Figure 4. Thermoelectric texture assessment in Ti-6Al-4V by four different experimental procedures.

opposite signs on the differently textured surfaces. After some searching, we have actually found a Ti-6Al-4V bar that separated the two sides ideally as it is shown in Figure 4d. Cooling resulted in better separation of textured materials because it eliminated the interface effects. Clearly, the demonstrated interface effect will also hinder the thermoelectric detection of any weak material variation caused by other phenomena such as work hardening, thermal shock, and high cycle fatigue.

The above approach was successfully used to detect cyclic plastic deformation in Ti-6Al-4V specimens. Figure 5 shows the probability density of the thermoelectric voltage produced by ≈-70 ^{o}C cooling at two different locations along a 1/4"x1"x8" Ti-6Al-4V bar that was cyclically deformed 10 times in a three-point bending configuration. Since thermoelectric testing is very sensitive to the chemical composition of the material, a Ti-6Al-4V reference bar from the same sample batch was used as the reference electrode. In order to assure that only the actual point of inspection was contributing to the measured thermoelectric signal, two long Ti-6Al-4V wires were used to connect the ends of the specimen and the reference electrode to the oscilloscope via an amplifier of 80 dB gain. A low-pass filter of 3 Hz cut-off frequency was used to reduce the electrical noise. The thermoelectric signal appeared to be a cumulative effect of plastic cycling as no significant separation was observed after the first loading. The "fatigued" signal was measured in the close vicinity of the maximum plastic deformation while the signals marked as "unfatigued" were taken close to the free ends of the specimen. Both locations were chosen on the same side of the rectangular bar in order to eliminate the potentially much larger differences caused by texture. The first crack was initiated after 30 cycles, i.e., 10 cycles correspond to 33% of the fatigue life before crack initiation. The maximum plastic strain near the loading point was app. 2%. The measured weak but statistically significant difference in thermoelectric power is a strong indication that thermoelectric measurements can be exploited to nondestructively detect increasing dislocation density and work hardening in Ti-6Al-4V. On the average, the fatigued and unfatigued portions of the specimen were bearing different signs, although the absolute difference was only 25 μV. The fatigued and unfatigued parts of the Ti-6Al-4V bar clearly exhibited some difference in thermoelectric power, although the sensitivity of this kind of inspection is still not high enough for practical nondestructive testing. Even the significant plastic deformation used

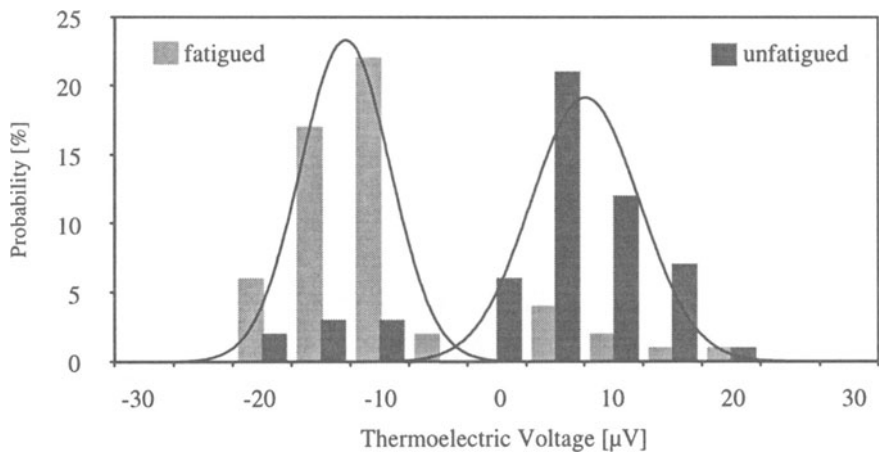

Figure 5. Experimentally determined probability density of the thermoelectric voltage produced by ≈70 ^{o}C cooling at two different locations along a 1/4"x1"x8" Ti-6Al-4V bar cyclically deformed 10 times in a three-point bending configuration.

in these experiments caused but a smaller difference in the thermoelectric power than texture. There were also several points in both unfatigued and fatigued portion that showed opposite sign with respect to the average, and the percentage of these locations of opposite sign was more than 10%. These variations were most probably caused by the relatively coarse grain structure or inevitable surface contamination.

DISCUSSION AND CONCLUSIONS

In conventional thermoelectric sorting one simply measures the voltage between a reference electrode and the specimen to be tested as the heat flows from the pre-heated reference electrode towards the specimen through the imperfect interface of the contact. Often, even when the reference electrode is of the same material as the specimen, a significant thermoelectric voltage will be produced by the inherent imperfection of the interface. Whenever such a thermoelectric tester is used to detect slight differences in thermoelectric power, this artifact can substantially offset the measured values. Simple compensation of the reported interface offset is rendered especially difficult by the fact that the offset voltage depends not only on the contact pressure but also indirectly on the size and shape of the specimen and reference electrode. On the other hand, the demonstrated intrinsic sensitivity of the thermoelectric technique to imperfect interfaces could be exploited for nondestructive evaluation of tightly compressed but metallurgically not bonded interfaces in spot welds, diffusion bonds, and other types of solid-state bonds and might lead to new inspection methods to detect distributed fatigue cracking in metals. The imperfect interface effect can be eliminated by symmetric cooling (or heating) that does not produce a significant temperature gradient through the junction to be inspected. We showed that this method, combined with an appropriate choice of the reference electrode, is capable of detecting not only texture but fatigue related material changes in titanium alloys.

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REFERENCES

1. E. B. Henry, C. M. Stuart, and W. Tomasulo, in *Nondestructive Testing Handbook* Vol. 9 (ASNT, Columbus, 1995) pp. 363-376.
2. P. M. Reynolds, J. Sci. Instr. 38, 313 (1961).
3. C. M. Stuart, in *Proc. 5th Ann. Int. Conf. NDE Nucl. Ind.* (1982) pp. 541-545.
4. C. M. Stuart, in *Intern. Adv. Nondestr. Testing* Vol. 9 (Gordon and Breach, 1983) pp. 177-192.
5. C. M. Stuart, J. Testing Eval. 15, 224 (1987).
6. W. Morgner, Mat. Eval. 9, 1081 (1991).
7. J. P. Fulton, B. Wincheski, and M. Namkung, in *Rev. Progr. Quant. Nondestr. Eval.* Vol. 13B (Plenum, New York, 1994) pp. 1,611-1,618.
8. R. H. Kropschot and F. J. Blatt, *Phys. Rev.* 116, 617 (1959).
9. P. B. Nagy and J. Hu, in *Review of Progress in QNDE*, Vol. 17, eds. D. O. Thompson and D. E. Chimenti (Plenum, New York, 1998) pp. 1573-1580.
10. J. Hu and P. B. Nagy, Appl. Phys. Lett. 73, 467 (1988).
11. *Titanium Alloys*, edited by R. Boyer, G. Welsch, and E. W. Collings (ASM International, Materials Park, 1994) p. 500.
12. M. Blodgett and P. B. Nagy, Appl. Phys. Lett. 72, 1045 (1998).